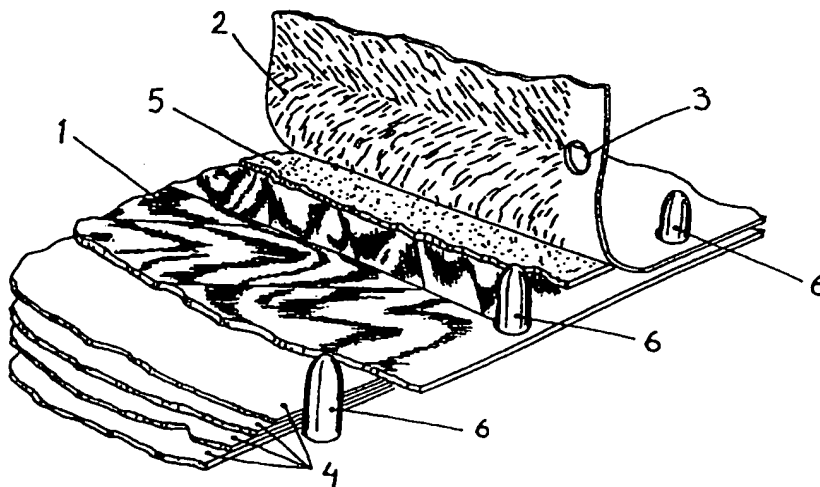




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(54) Title: A PROCESS FOR THE MANUFACTURE OF A DECORATIVE LAMINATE



(57) Abstract

A process for the manufacture of a decorative thermosetting laminate (21), which laminate (21) includes thermosetting resin impregnated paper layers. A decor paper in the form of a web or a sheet (11, 1) is provided with a decor pattern including pattern sections with different directions. The decor paper (11, 1), which is preferably impregnated with melamine-formaldehyde resin, is placed as a surface layer on a base layer and bonded thereto by pressing under elevated pressure. A matrix provided with a number of surface-structure sections intended to at least mainly coincide with corresponding decor pattern sections of the decor paper (1, 11) is used. The matrix is accurately placed on top of the decor paper before the pressing and is after the pressing separated from the obtained laminate (21), wherein the laminate (21) will get a decor surface with a surface structure which corresponds to the decor.

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A process for the manufacture of a decorative laminate.

The present invention relates to a process for the manufacture of a decorative thermosetting laminate with a surface structure that realistically matches the decor of the upper surface.

Products coated with thermosetting laminates are frequent today. They are foremost used where the demand for abrasion resistance is high, but also where resistance towards different chemicals and moisture is required. As an example of such products floors, floor beadings, table tops, work tops and wall panels can be mentioned.

The thermosetting laminate mostly consists of a number of base sheets with a decor sheet placed closest to the surface. The decor sheet can be provided with a desired decor or pattern. The most frequent patterns usually represent the image of different kinds of wood, or minerals such as marble or granite. The surface of the laminate can be provided with a structure during the laminating procedure which will make the decor more realistic. Press plates with structure or structure foils are frequently used when manufacturing such a laminate. A negative reproduction of the structure in the press plate or the foil will be imprinted into the laminate during the laminating procedure.

The structure suitably represents features characteristic for the pattern the decor represents in the laminate. The structure can be made coarse to simulate for example roughly planed stone, or smooth with randomly placed pits and micro cracks to simulate polished marble. A wood surface is simulated by providing the surface with randomly placed thin oblong indentations which imitate pores. These indentations must be oriented in the direction of the growth of the simulated wood, which is indicated by the pattern of the graining, in order to make the result realistic. Therefore the graining and the simulated pores are oriented only in the longitudinal direction of the laminate. Since thermosetting laminates are often used on large surfaces as for example floors, it is essential that the pattern doesn't repeat itself. This is achieved by making a random pattern in the floor or by repeating the pattern with a low repetition frequency.

It has for a long time been a great need to be able to manufacture a decorative thermosetting laminate with a decor pattern for example with decor sections directed in different directions and with a matching surface structure. Such a pattern simulates for example boards or bars placed in different directions. Since it

has been impossible to provide these patterns with a matching surface structure these patterns have been avoided or provided with a smooth surface.

According to the present invention the above mentioned needs have been met and a thermosetting laminate with a decorative surface with a matching surface structure has been achieved. The invention relates to a process for the manufacture of a decorative thermosetting laminate, which laminate includes thermosetting resin impregnated paper layers. A decor paper in the form of a web or a sheet, provided with a decor pattern having pattern sections with different directions and impregnated with a thermosetting resin, preferably melamine-formaldehyde resin which has then been dried, is placed as a surface layer on a base layer and bonded thereto by pressing under elevated pressure. The invention is characterised in that a matrix is used, which matrix is provided with a number of surface-structure sections being structurally independent from each other. The surface structure sections are intended to at least mainly but preferably completely coincide with corresponding decor sections of the decor paper. The matrix is accurately placed on top of the decor paper before the pressing and is after the pressing separated from the laminate obtained. The laminate will hereby get a decor surface with a surface structure, the different directions of which corresponds with the directions of the different decor sections of the decor pattern. By this process also characteristic deviations in the pattern as for example twigs and the like in wood patterns can be provided with a realistic surface structure.

According to one embodiment of the invention the base layer consists of a number of conventional dry base layer paper webs or base layer paper sheets, impregnated with thermosetting resin. The resin in the uppermost of these is possibly melamine-formaldehyde resin. The rest of the webs or sheets, contains phenol-formaldehyde resin. The decor paper web or decor paper sheet, is placed on top of the conventional base layer webs or base layer sheets. The different paper webs or a stack of sheets are then, continuously or discontinuously respectively laminated together at an elevated pressure and an elevated temperature. The different papers will hereby be bonded to one another.

At the drying of the above resin impregnated paper webs the solvent is evaporated and the resin is partially cured to a so called B-stage. The impregnated paper obtained is usually called pre-preg.

According to another embodiment of the invention the base layer consists of a particle board or a fibre board. Hereby for example a table top or a laminate floor

can be produced at the same time as the lamination of the thermosetting laminate, wherein an extra stage in the manufacturing can be avoided.

The matrix preferably consists of a structure foil, a press plate or the like which have been provided with the desired structure pattern. When the pattern in the decor paper has been designed, this design is suitably used as a base when manufacturing the structure foil. Hereby a three-dimensional structure which completely or partially coincides with the pattern of the decor can be achieved.

The decor paper web or decor paper sheets respectively are preferably provided with positioning means such as colour dots, holes, code lines, indentations or the like. The positioning means are placed in a predetermined relation to the direction variations of the decor pattern. The matrix is preferably also provided with positioning means such as colour dots, holes, code lines, indentations or the like. These positioning means are placed in a predetermined relation to the borders of the surface structure sections. The positioning means in the matrix and in decor paper respectively, are preferably mutually, so that an accurate match between decor and surface structure is achieved by placing the positioning means toward each other.

The decor pattern can, for example, consist of a number of sections of parallel rows of bars, where the bars in adjoining rows are preferably mutually offset in the longitudinal direction. One section of bars is thereby arranged parallel to the longitudinal direction of the laminate and followed by a section of bars arranged perpendicular to the previous section of bars and so on.

A tolerance area is suitably used on the matrix in the demarcation between two adjacent, of each other independent, surface structure sections. The tolerance area consists of a 1 - 20 mm wide, preferably 3 - 10 mm wide, field without any structure.

According to another embodiment a tolerance area is used on the matrix in the demarcation between two adjacent, of each other independent, surface structure sections. This tolerance area consists of a 1 - 20 mm wide, preferably 3 - 10 mm wide, field where the first structure is gradually transformed into the other surface structure.

The surface layer of the laminate suitably includes a so-called overlay paper, preferably of alfa-cellulose, placed on top of the decor paper. Hereby the useful life of the laminate is extended since the overlay paper has to be worn down before a visible wear of the decor sheet takes place. The overlay paper is suitably

impregnated with melamine-formaldehyde resin. Suitably at least one of the thermosetting resin impregnated sheets, preferably the uppermost one is coated with hard particles for example of silica, aluminium oxide and/or silicon carbide with an average size of 1 - 100 μm , preferably around 5 - 60 μm . Hereby the wear resistance is increased even further.

The lamination preferably takes place in a continuous laminate press with two steel belts wherein the matrix consists of a structure foil which preferably has the form of a closed web which is continuously fed through the press. The pressure in the press is suitably 5 - 90 Bar, preferably 20 - 70 Bar. The temperature is suitably 140 - 200°C, preferably 160 - 180°C. The velocity of the matrix and/or the decor paper web is preferably continuously guided. This is suitably achieved by means of sensors such as mechanical transmitter, scanners, photocells, ccd cameras, pneumatic sensors or the like and the positioning means so that an accurate match between the decor and surface structure is obtained. At discontinuous lamination suitably a multi-opening press is used, in which many laminates can be produced simultaneously. The pressure is then usually 20 - 150 Bar, preferably 70 - 120 Bar and the temperature suitably 120 - 180°C, preferably 140 - 160°C.

The invention is further explained in connection to the accompanying drawings showing different embodiments of the invention where.

-Figure 1 shows parts of a number of base layer sheets, one decor sheet, one overlay sheet and a matrix in the form of a structure foil. The sheets and the foil have been stacked before a pressing in a discontinuous laminate press of multi-opening type.

-Figure 2 shows schematically a continuous lamination procedure according to the invention.

Figure 1 shows a bundle where a number of different sheets have been stacked before a pressing. The bundle consists from bottom to top of

- a) a number of base layer sheets 4 which are impregnated with phenol-formaldehyde resin,
- b) one base layer sheet 4' which is impregnated with melamine-formaldehyde resin,
- c) one decor paper sheet 1 containing pattern sections with stopping directions, which sheet is impregnated with melamine-formaldehyde resin,
- d) one so-called overlay paper sheet 5 of α -cellulose impregnated with melamine-formaldehyde resin and coated with hard particles of silicon carbide with an average size of 50 μm ,

e) one matrix in the form of a structure foil sheet 2 with different surface structure sections directed in different directions. The decor sheet 1 and the structure foil sheet 2 are cut so that the decor sections and the structure sections are fairly matched. The decor sheet 1 and the structure foil sheet 2, which are provided with positioning means in the form of holes 3 along both of their long sides are somewhat wider than the other sheets of the bundle. The holes 3, whose centre corresponds to the change of direction in the structure and the decor, will thereby be located outside the long side edges of the other sheets 4, 4' and 5. The decor sheet 1 and the structure foil sheet 2 will be accurately matched by threading them on to a number of guiding rods 6 whose diameter is adapted to the diameter of the holes 3. The other sheets 4, 4' and 5 are oriented by being supported by the inner edges of the guiding rods. Between each of these so called press bundles a flat press plate is placed. When the desired number of press bundles and press plates have been stacked, the bundles are moved to a multi-opening press, where the sheets in the respective press bundle are laminated together at a pressure of 90 Bar and a temperature of 150°C for 60 minutes. The structure foils 2 are after the pressing separated from the completed laminates.

The bundles can, besides being laminated together in a multi-opening press, also be laminated together in a continuous laminate press. The sheets in the press bundles are then suitably first bonded together via their edges, after which the bundles one by one are fed in between two steel belts in the continuous laminate press, where they are laminated. The above mentioned intermediate press plates are excluded when using this method. The sheets in a press bundle can be welded together by locally pressing them together in a number of points while heating so that the resin melts locally. By using this method the sheets in a bundle will be prevented from sliding while handling before pressing.

Figure 2 shows schematically a continuous lamination procedure where a number of different paper webs from rolls are feed into a continuous laminate press 20 provided with two continuous steel belts 22 between which the different paper webs are laminated together. The webs consists from below to top of:

- a) a number of base paper webs 14 which are impregnated with phenol-formaldehyde resin,
- b) one base paper web 14' which is impregnated with melamine-formaldehyde resin,
- c) one decor paper web 11 containing decorative pattern sections with different directions which web is impregnated with melamine-formaldehyde resin,
- d) one matrix in the form of a structure foil web 12 with different surface structure sections. The decor web 11 and the structure foil web 12 are at their

outer edges provided with positioning means 3 in the form of code lines. The velocity of the decor web 11 and the structure foil web 12 is guided via clamp rollers 18', 18. The velocity of the clamp rollers 18, 18' is guided via two optical sensors 19 which detect the mutual position of the code lines on the decor web 11 and the structure foil web 12. The code lines are placed at a predetermined relation to the borders of the surface structure sections on the structure foil web 12 as well as pattern sections of the decor web 11. The surface structure and decor can hereby be accurately matched before the pressing is initiated. The different webs are continuously laminated together in a continuous laminate press 20 at a pressure of 35 Bar and a temperature of 180°C. The structure foil web 12 is after the pressing separated from the completed laminate 21.

The structure foil web 12 can alternatively be cut into sheets. These structure foil sheets will then one by one be accurately positioned on top of the decor paper web 11 by means of the code lines and feed into the continuous laminate press 20. It is also possible to cut the decor paper web 11 into sheets instead of the structure foil web 12. The decor paper sheets will then one by one be positioned under the structure foil web 12 by means of the code lines and feed into the continuous laminate press 20. The positioning of the structure foil sheets or the decor paper sheets can be made either automatically or manually. It is also possible to make a bundle of the uppermost sheets as described together with figure 1. These bundles can for example consist of from bottom to top; a decor paper sheet 1, an overlay sheet 5 and a structure foil sheet 2. The accurate positioning between decor and structure will be made when the bundles are made. The bundles will then one by one be placed on top of the base paper web 14' and feed into the continuous laminate press 20. This alternative method can be used when the normal method of matching adjustments becomes insufficient, due to for example large differences in thermal expansion, moisture expansion or very high demands for an exact match between the structure foil web 12 and the decor paper web 11.

The invention is not limited by the shown embodiments since they can be varied in different ways within the scope of the invention. The structure foil web 12 according to the embodiment described together with figure 2 can for example be replaced by one of the press belts 22 of the laminate press 20, by providing this with different structure sections. The press belt can further be provided with a number of dowels at its edges, which dowels corresponds to holes placed at the edge of the decor web 11. If a surface structure foil web 12 is used, this is suitably also provided with corresponding holes at its edges. The webs can hereby be oriented and fed like computer paper with so called tractor feeding in a printer. Likewise also the surface structure foil sheet can in the embodiment described in




figure 1 be replaced by a press plate which has been provided with corresponding different surface structure sections.

CLAIMS

1. A process for the manufacture of a decorative thermosetting laminate (21), which laminate (21) includes thermosetting resin impregnated paper layers, wherein a decor paper in the form of a web or a sheet (11 and 1 respectively), provided with a decor pattern having pattern sections with different directions, and impregnated with a thermosetting resin, preferably melamine-formaldehyde resin which resin has then been dried, is placed as a surface layer on a base layer and bonded thereto by pressing under elevated pressure, characterised in that a matrix (12 and 2 respectively), provided with a number of surface-structure sections being structurally independent from each other and intended to at least mainly but preferably completely coincide with corresponding decor sections of the decor paper (1, 11), is accurately placed on top of the decor paper before the pressing and is after the pressing separated from the laminate (21) obtained, wherein the laminate (21) will get a decor surface with a surface structure, the different directions of which correspond with the directions of the different decor sections of the decor pattern.
2. Process according to claim 1 characterised in that the base layer consists of a number of conventional dry base layer paper webs (14, 14') or base layer paper sheets (4, 4') which are impregnated with a thermosetting resin wherein the resin in the uppermost (14' and 4' respectively) of these possibly is melamine-formaldehyde resin while the rest of the webs or sheets preferably contain phenol-formaldehyde resin, wherein the decor paper web (11) or decor paper sheet (1) respectively, is placed on top of the conventional base layer webs (14, 14') or base layer sheets (4, 4') after which the different paper webs or a stack of sheets respectively are continuously or discontinuously laminated together at an elevated pressure and an elevated temperature.
3. Process according to claim 1 characterised in that the base layer consists of a particle board or a fibre board.
4. Process according to any of the claims 1 - 3 characterised in that the matrix consists of a structure foil, a press plate or the like (12, 2) which have been provided with the desired structure pattern.
5. Process according to any of the claims 1 - 4 characterised in that the decor paper web (11) or decor paper sheet (1) respectively, has positioning means (3) such as colour dots, holes, code lines, indentations or the like, and that said positioning means (3) are placed in a predetermined relation to the direction variations of the decor pattern.

6. Process according to any of the claims 1 - 5 characterised in that the matrix (12, 2) is provided with positioning means (3) such as colour dots, holes, code lines, indentations or the like, and that said positioning means (3) are placed in a predetermined relation to the borders of the surface structure sections.
7. Process according to claim 5 or 6 characterised in that the positioning means (3) in the matrix and decor paper (1, 11) respectively, are mutually matched, so that by placing them toward each other an accurate match between decor and surface structure is achieved.
8. Process according to any of the claims 1 - 7 characterised in that the decor pattern consists of a number of sections of parallel rows of bars, where the bars in adjoining rows are preferably mutually offset in the longitudinal direction, wherein one section of bars arranged parallel to the longitudinal direction of the laminate is followed by a section of bars arranged perpendicular to the previous section of bars.
9. Process according to any of the claims 1 - 8 characterised in that a tolerance area is used on the matrix in the demarcation between two adjacent, of each other independent, surface structure sections, which tolerance area consists of a 1 - 20 mm wide, preferably 3 - 10 mm wide, field without any structure.
10. Process according to any of the claims 1 - 8 characterised in that a tolerance area is used on the matrix in the demarcation between two adjacent, of each other independent, surface structure sections, which tolerance area consists of a 1 - 20 mm wide, preferably 3 - 10 mm wide, field where the first surface structure is gradually transformed into the second surface structure.
11. Process according to any of the claims 1 - 10 characterised in that the surface layer of the laminate includes a so called overlay paper (5), preferably of alfa-cellulose, placed on top of the decor paper (1, 11).
12. Process according to claim 11 characterised in that the overlay paper (5) is impregnated with melamine-formaldehyde resin.
13. Process according to any of the claims 2 - 12 characterised in that the lamination takes place in a continuous laminate press (20) wherein the matrix consists of a structure foil (12) which preferably has the form of a closed web which is continuously fed through the press.
14. Process according to claim 12 characterised in that the pressure in the press is 5 - 90 Bar, preferably 20 - 70 Bar, and that the temperature is 140 - 200°C, preferably 160 - 180°C.

15. Process according to any of the claims 1 - 14 characterised in that velocity of the matrix and/or the decor paper web is continuously guided by means of sensors such as mechanical transmitters, scanners, photocells, ccd cameras, pneumatic sensors or the like (19) and the positioning means (3) so that an accurate match between the decor and surface structure is obtained.
16. Process according to any of the claims 1 - 15 characterised in that at least one of the thermosetting resin impregnated sheets, preferably the uppermost one is coated with hard particles, for example silica, aluminium oxide and/or silicon carbide with an average size of 1 - 100 μm , preferably around 5 - 60 μm .

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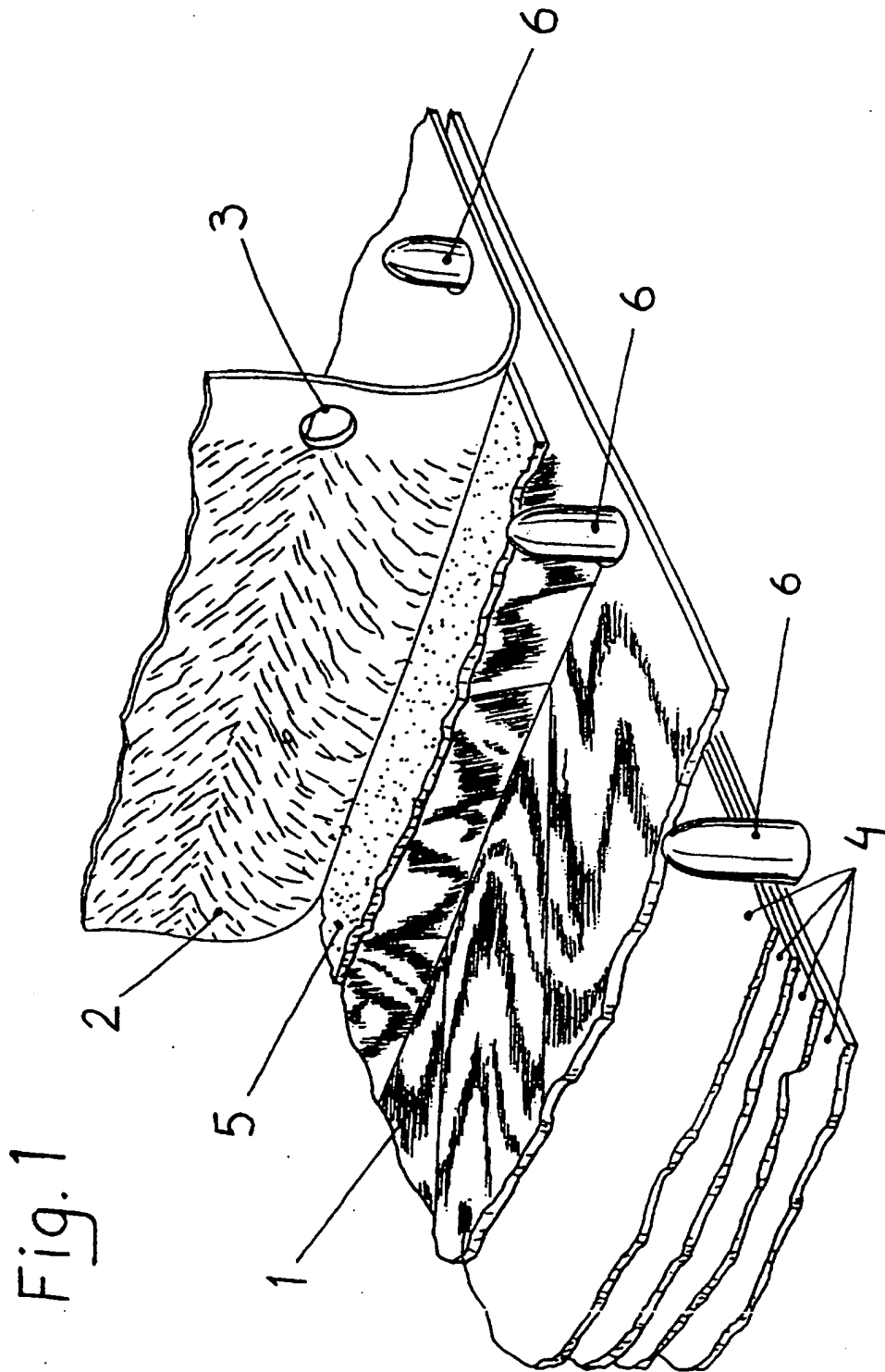
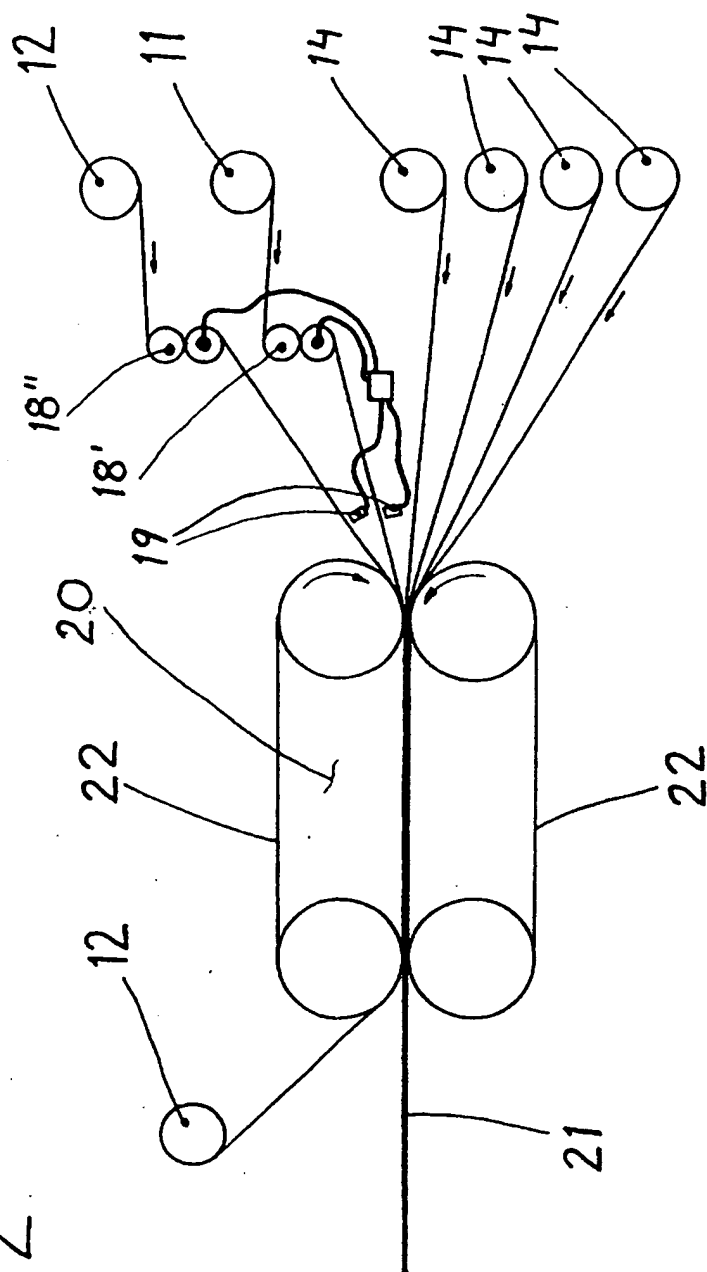


Fig. 1

Fig. 2



INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 97/00310

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: B32B 27/04, B32B 29/00, B32B 31/12, B44C 5/04
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Minimum documentation searched (classification system followed by classification symbols)

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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

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RM25, EPODOC, WPI

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|--|-----------------------|
| A | US 3698978 A (JOHN E. MCQUADE, JR.), 17 October 1972 (17.10.72) | 1 |
| A | US 3654044 A (HATSUO HIROTA), 4 April 1972 (04.04.72) | 1 |
| A | US 3648358 A (CANNADY, JR. ET AL), 14 March 1972 (14.03.72) | 1 |
| A | US 3373068 A (GENE EDWARD GROSHEIM ET AL), 12 March 1968 (12.03.68) | 1 |

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INTERNATIONAL SEARCH REPORT

Information on patent family members

20/05/97

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| Patent document cited in search report | | | Publication date | Patent family member(s) | | Publication date |
|---|---------|---|---------------------|----------------------------|----------|---------------------|
| US | 3698978 | A | 17/10/72 | NONE | | |
| US | 3654044 | A | 04/04/72 | NONE | | |
| US | 3648358 | A | 14/03/72 | BE | 757954 A | 01/04/71 |
| | | | | CA | 941284 A | 05/02/74 |
| US | 3373068 | A | 12/03/68 | NONE | | |